Chitosan-Based Nanocomposite Beads for Drinking Water Production

ML Masheane[1,2], LN Nthunya[1,2], SS Sambaza[2], SP Malinga[2], EN Nxumalo[1], BB Mamba[1] and SD Mhlanga[1*]
[1]Nanotechnology and Water Sustainability Research Unit, College of Science, Engineering and Technology, University of South Africa, Florida, 1709, Johannesburg, South Africa.
[2]Department of Applied Chemistry and the DST/Mintek Nanotechnology Innovation Centre-Water Research Node, University of Johannesburg, P.O. Box 17011, Doornfontein, 2028, South Africa.

E-mail: mhlansd@unisa.ac.za

Abstract. Potable drinking water is essential for the good health of humans and it is a critical feedstock in a variety of industries such as food and pharmaceutical industries. For the first time, chitosan-alumina/functionalised multiwalled carbon nanotube (f-MWCNT) nanocomposite beads were developed and investigated for the reduction of various physico-chemical parameters from water samples collected from open wells used for drinking purposes by a rural community in South Africa. The water samples were analysed before and after the reduction of the identified contaminants by the nanocomposite beads. The nanocomposite beads were effective in the removal of nitrate, chromium and other physico-chemical parameters. Although, the water samples contained these contaminants within the WHO and SANS241 limits for no risk, the long-term exposure and accumulation is an environmental and health concern. The reduction of these contaminants was dependent on pH levels. At lower pH, the reduction was significantly higher, up to 99.2% (SPC), 91.0% (DOC), 92.2% (DO), 92.2% (turbidity), 96.5% (nitrate) and 97.7% (chromium). Generally, the chitosan-alumina/f-MWCNT nanocomposite beads offer a promising alternative material for reduction and removal of various physico-chemical parameters for production portable water.

Key words: Beads, carbon nanotubes, chitosan, nanocomposites, water purification

1. Introduction

The contamination of water resources by toxic molecules of organic, inorganic and biological nature is currently the world's major concern. Potable water production from surface and groundwater sources normally implicates the use of water treatment processes that remove turbidity, bacteria, colour, organic compounds and clay particles. These suspended materials are of environmental concern and pose a serious threat to water quality consumed by societies globally (Bina et al. 2009). Hence, these contaminants must be adequately removed from water in order to produce potable water and to comply with stringent environmental quality standards. Recently, there has been a significant interest in the development of non-toxic, biocompatible and biodegradable biopolymers such as chitosan, that can used in water treatment (No and Meyers 2000).

Chitosan is a natural linear biopolyaminosaccharide obtained by the alkaline deacetylation of chitin, which is the principal component of protective cuticles of crustaceans such as crabs, shrimps, prawns and lobsters. It is a weak base that is insoluble in water and in organic solvent but soluble in dilute

[*] To whom correspondence should be addressed - email: mhlansd@unisa.ac.za

aqueous acidic solutions (pH < 6.5), which can convert glucosamine units into soluble forming R–NH_3^+ (Dutta et al. 2004). Chitosan has recently emerged as a low-cost biosorbents for the removal of heavy metals, organics and micro-organisms. Although it is cost effective and non-toxic, it is unstable in harsh conditions such as low pH levels and higher temperatures. To overcome this challenge, scientists have focussed on its modification. The presence of three of the reactive groups on chitosan, an amino group at C-2 position, as well as the primary and secondary hydroxyl groups at C-6 and C-3 positions, respectively make this material very susceptible to chemical modification such as acetylation, N-phthaloylation, tosylation, alkylation and graft polymerization (Olteanu 2007). Modification of chitosan with inorganic materials is of research interest.

The objective of this work was to synthesize a novel adsorbent, chitosan-alumina/functionalised multiwalled carbon nanotube (f-MWCNT) nanocomposite beads for the removal of total chromium and nitrates from water. The physico-chemical parameters such as electrical conductivity, turbidity and total dissolved solutes were also studied to ascertain the validity of the nanocomposite beads for the removal of chromium and nitrates from water.

2. Experimental

2.1. Materials

Chitosan (degree of deacetylation= 85%), sodium nitrate, potassium dichromate, alumina (particle size in the range of 30-60 nm), sodium hydroxide, hydrochloric acid, oxalic acid, nitric acid and sulfuric acid were purchased from Sigma Aldrich. MWCNTs were synthesised and acid treated in our laboratory using the procedure by Mhlanga et al. 2009. Deionized water was obtained from a water purification system (Po process Ecopure G.I.I Scientific) available in our laboratories.

2.2. Preparation of chitosan-alumina/f-MWCNT nanocomposite beads

Chitosan gel (2%) was prepared using a modified procedure reported by Ngah and Fatinathan 2010, and Chatterjee and Woo 2009. Chitosan powder (2 g) was dissolved into 100 ml of 5% oxalic acid and stirred for 12 h. Then 0.2 g alumina and 0.1 g f-MWCNTs were added while stirring. The homogeneous gel was de-gassed and added dropwise into a precipitation bath containing 2 M sodium hydroxide solution by using a 0.4 mm cut diameter syringe needle and vigorously stirred using a magnetic stirrer. After a few seconds, black coloured beads formed, and they were collected and washed with distilled water until pH 7 was attained. The beads were dried in the oven at 60 °C overnight prior to use.

2.3. Batch adsorption experiments

The experiments were conducted in a 250 mL conical flask containing 100 mL of natural water samples using 1 g of chitosan and chitosan based nanocomposite beads. The flask and its contents were agitated at room temperature using a linear shaker. The effect of pH was studied at various pH levels ranging from pH 2 – 8 at the 1 g/100 mL beads dosage for 60 min contact time. Finally, the effect of contact time on the removal efficiency was investigated in the range of 5 – 240 min. After the experiment, the mixtures were then filtered and the concentrations of total chromium and nitrate were analysed using an inductively coupled plasma optical emission (ICP-OES) ICAP 6000 series spectrometer thermos Fisher-Scientic and Dionex Ion Chromatography 2000 (IC) spectroscopy respectively. The removal efficiency of nitrates, total chromium and various physico-chemical parameters was calculated using **Equation 1** (Jagtap et al. 2011):

$$\% \text{ Removal} = \frac{C_i - C_e}{C_i} \times 100 \tag{1}$$

where C_i and C_e are the initial and final concentrations (g/mL), respectively.

2.4. Sampling
The water samples were collected from a shallow well in rural community (Lochiel) in Mpumalanga province in South Africa. This well is used by the community for drinking and other domestic purposes. The water samples were collected in plastic containers which were sterilised with methanol, and carried in a cooler box to laboratory, where they were stored in the refrigerator at 4 °C. The samples were also analysed on-site for dissolved oxygen (DO), electrical conductivity, pH, temperature and alkalinity using Hanna Instrument multi-meter (model Hi-9828).

3. Results and discussion

3.1. Physical properties of chitosan-alumina/f-MWCNT nanocomposite beads
Figure 1 shows the chitosan-alumina/f-MWCNT nanocomposite beads. The nanocomposite beads were black in colour due to the presence of black functionalised MWCNTs. The nanocomposite beads were ellipsoidal in shape with an average diameter (size) in the range of 3 – 5 mm.

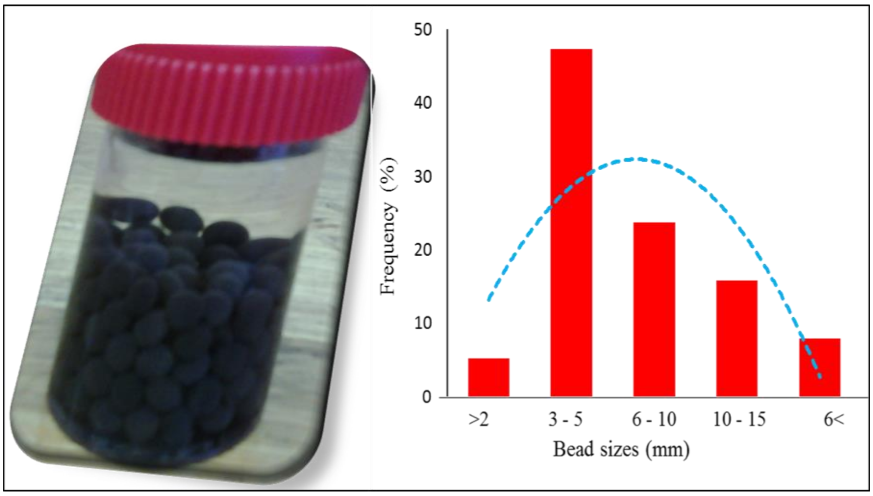

Figure 1: Chitosan-alumina/f-MWCNT nanocomposite beads. Insert is the average diameter (size) of the nanocomposite beads.

3.2. Reduction of physico-chemical properties by chitosan-based nanocomposite beads
The physical characteristics of water used by the community of Lochiel in Mpumalanga are presented in **Table 1**. Generally, the results of the analysis demonstrated that water samples collected from one of drinking water sources in Lochiel (shallow well) were within the WHO and the Department of Water Affair and Sanitation recommended limits for drinking water quality specifications for no risk in terms of pH (5 – 9), turbidity (< 5 NTU), DOC (< 8.2 mg/L), DO (< 1000 mg/L), chromium (< 100 µm/L), nitrate (< 6 mg/L) and SPC (< 150 µS/cm) (WHO 2011; SANS 2006). The reduction of these physico-chemical properties using chitosan- alumina/f-MWCNT nanocomposite beads was significantly high. The concentration of SPC, DOC, DO, nitrates and chromium drop from 26.8, 0.87, 8.71, 0.26 and 0.8 mg/L to 0.67, 0.10, 0.73, 0.01 and 0.02 mg/L, respectively. Turbidity also decreased from 4.62 to 0.05 NTU while pH was increased from 6.27 to 7.08, mainly because metals act as Lewis acids and their removal decrease acidity. Therefore, it is obvious that parameters were reduced largely by chitosan-alumina/f-MWCNT nanocomposite beads.

IOP Conf. Series: Materials Science and Engineering **195** (2017) 012004 doi:10.1088/1757-899X/195/1/012004

Table 1: Physico-chemical characteristics of raw and treated water from Lochiel.

Parameters	Raw Water	Treated water	%Removal
SPC (μS/cm)	26.84	0.67	97.51
pH	6.27	7.08	N/A
DOC (mg/L)	0.87	0.10	88.28
DO (%)	8.71	0.73	91.58
Turbidity (NTU)	4.62	0.05	98.97
Nitrates (mg/L)	0.26	0.00	98.17
Chromium (mg/L)	0.80	0.01	97.72

3.3. Effect of pH on the reduction of physico-chemical properties

pH is an important parameter that has a significant effect on the adsorption of species on the adsorbents. The effect of pH of water samples on the chitosan-alumina/f-MWCNT nanocomposite beads was investigated at pH range of pH 2 – 8 (Figure 2). It was observed that the reduction of physico-chemical parameters was higher at lower pH levels, and was decreased slightly with increasing pH values. The increase in the amount of nitrates adsorbed at low pH was attributed to protonation of some amino (-NH_2) groups from chitosan and hydroxyl (-OH^-) groups from either chitosan, alumina or f-MWCNTs. The protonation of the active sites significantly enhanced the electrostatic interactions between positively charged adsorbent surface and negatively charged sorbates (nitrates, dichromate). This was also observed by Demiral and Gündüzoğlu 2010 on positive impact of low pH on nitrates adsorption by activated carbon. **Equations 2 and 3** represent the protonation of -NH_2 and -OH^- groups and removal of nitrates from aqueous media. The lower pH values cause the surface hydroxyl (-OH^-) groups to accept proton (H^+), thus facilitating the ligand exchange since water (H_2O) is a weak ligand than -OH to get displaced from adsorbent bonding sites. Basically, the lower pH levels promote the adsorption of anions, *i.e.* at low pH, a large number of hydrogen ions (H^+) can neutralise the oppositely charged surface and thus enhance the electrostatic attraction between the adsorbent and adsorbate, overcoming electrostatic repulsion between them (Alemayehu et al. 2012). Furthermore, at lower pH, the spontaneous reduction of chromium (VI) to chromium (III) was because of reduction-oxidation potential (13.4 mV), thus resulting to up to 97.7% chromium removal (Nithya and Sudha 2017).

$$-NH_2 + H^+ \rightarrow -NH_3^+ + NO_3^- \rightarrow -NH_3^+ \cdots\cdots NO_3^- \quad (2)$$

$$-OH^- + 3H^+ \rightarrow -OH_3^+ + NO_3^- \rightarrow -OH_3^+ \cdots\cdots NO_3^- \quad (3)$$

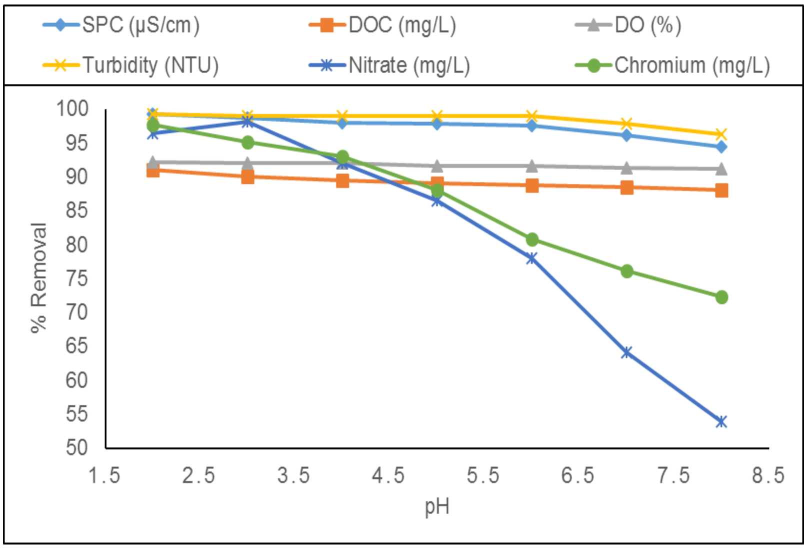

Figure 2: The effect of pH on the reduction of physico-chemical pamarameter using 1 g of chitosan-alumina/f-MWCNT nanocomposite beads at constant contact time (60 min).

3.4. Effect of contact time on the reduction of physico-chemical parameters

The effect of contact time on the reduction of physico-chemical properties by chitosan-alumina/f-MWCNT nanocomposite beads was investigated at 0 - 240 min time interval at pH 6 as shown in **Figure 3**. It was observed that there was a rapid reduction of physico-chemical parameters within the first 30 min and equilibrium water reached within 60 min. After 60 min, there is no significant change in the reduction of the physico-chemical reduction, meaning that the adsorbent active sites were being saturated. The highest reduction efficiencies for physico-chemical parameters achieved were 99.12% (SPC), 90.22% (DOC), 91.90% (DO), 99.85% (turbidity), 98.01% (nitrate) and 82.03% (chromium).

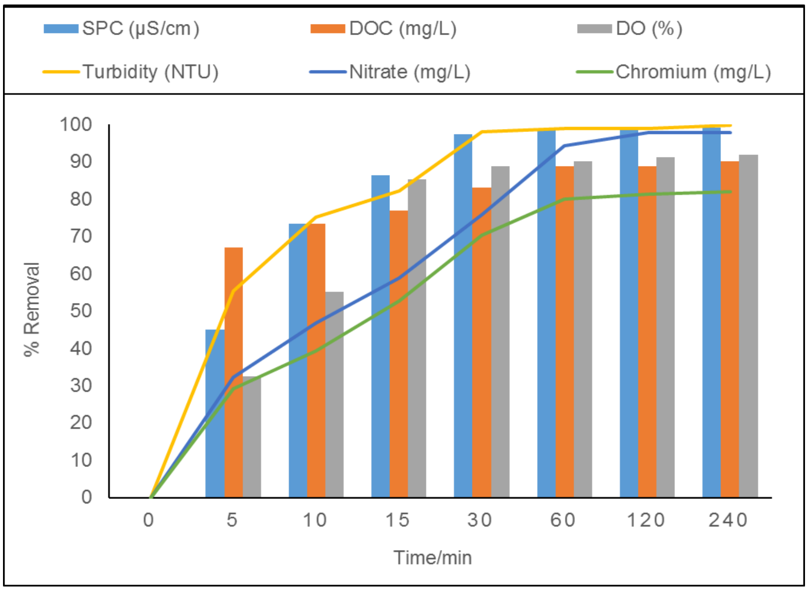

Figure 3: The effect of contact time on the removal of physico-chemical parameters by 1 g of chitosan-alumina/f-MWCNT nanocomposite beads.

4. Conclusions

The quality water samples collected from a shallow well used for drinking and other domestic purposes in a selected community in the Mpumalanga province, South Africa was found to be within WHO and SANS limit for no risk from drinking in terms of physico-chemical parameters including SPC, DO, DOC, turbidity, nitrates and chromium. However, the accumulation and long-term exposure of these physico-chemical properties is of environmental and health concern. For instance, long-term exposure and accumulation of chromium has chronic health effect (cancer). The newly development chitosan-alumina/f-MWCNT nanocomposite beads were effective in removal nitrate and chromium as well as reduction of other physico-chemical parameters. The reduction of these parameters was dependent on pH levels. At lower pH level the reduction was significantly higher, up to 99.2% (SPC), 91.0% (DOC), 92.2% (DO), 92.2% (turbidity), 96.5% (nitrate) and 97.7 % (chromium). The removal of the physico-chemical parameters was rapid in the first 30 min and insignificant beyond 60 min, due to saturation of the active sites. Generally, the chitosan-alumina/f-MWCNT nanocomposite beads can be employed in water treatment for reduction of various physico-chemical parameters.

Acknowledgements

The authors wish to thank (DST)/NRF Nanotechnology Flagship project (No 88046), the Water Research Commission, DST/Mintek Nanotechnology Innovation Centre (NIC), the Department of Applied Chemistry (University of Johannesburg), and the Nanotechnology and Water Sustainability (NanoWS) Research Unit for supporting this work. Part of this work was extraced from the masters dissertation of the first author, ML Masheane.

References

Alemayehu, D.D., Singh, S.K. and Tessema, D.A., 2012. Assessment of the adsorption capacities of fired clay soils from Jimma (Ethiopia) for the removal of Cr (VI) from aqueous solution. *Universal J. Environ. Res. Technol.*, 2(5), pp.411–420.

Bina, B., Mehdinejad, M.H., Nikaeen, M. and Attar, H.M., 2009. Effectiveness of chitosan as natural coagulant aid in treating turbid waters. *Iran. J. Environ. Health. Sci. Eng.*, 6(4), pp.247–252.

Chatterjee, S. and Woo, S.H., 2009. The removal of nitrate from aqueous solutions by chitosan hydrogel beads. *J. Hazard. Mater.*, 164(2-3), pp.1012–1018.

Demiral, H. and Gündüzoğlu, G., 2010. Removal of nitrate from aqueous solutions by activated carbon prepared from sugar beet bagasse. *Bioresour. Technol.*, 101(6), pp.1675–1680.

Dutta, P.K., Dutta, J. and Tripathi, V.S., 2004. Chitin and chitosan: Chemistry, properties and applications. *J. Sci. Industr. Res.*, 63(January), pp.20–31.

Jagtap, S., Yenkie, M.K.N., Labhsetwar, N. and Rayalu, S., 2011. Defluoridation of drinking water using chitosan based mesoporous alumina. *Micropor. Mesopor. Mater.*, 142(2-3), pp.454–463.

Mhlanga, S.D., Mondal, K., Carter, R., Witcomb, M.J. and Coville, N.J., 2009. The effect of synthesis parameters on the catalytic synthesis of multiwalled carbon nanotubes using Fe-Co/$CaCO_3$ catalysts. *S. Afr. J. Chem.*, 62, pp.67–76.

Ngah, W.S.W. and Fatinathan, S., 2010. Pb(II) biosorption using chitosan and chitosan derivatives beads: Equilibrium, ion exchange and mechanism studies. *J. Environ. Sci.*, 22(3), pp.338–346.

Nithya, R. and Sudha, P.N., 2016. Removal of heavy metals from tannery effluent using chitosan-g-poly(butyl acrylate)/bentonite nanocomposite as an adsorbent. *Textil. Cloth. Sustainability*, 2(1), p.1-7.

No, H.K. and Meyers, S.P., 2000. Application of chitosan for treatment of wastewaters. *Rev. Environ. Contamin. Toxicol.*, 163(1976), pp.1–27.

Olteanu, C.E., 2007. Applications of functionalized chitosan. *Sci. Stud. Res.*, 3, pp.227–256.

SANS-241, 2006. South African National Standard: Drinking water-drinking water. Published by Standards South African, a division of SABS. ISBN 0-626-17752-9.

WHO, 2011. World Health Organization. Guideline for drinking water quality. 20 Avenue Appia, 1211 Geneva 27, Swirtzerland.